REMARKS

The claims have been rewritten to better define the claimed invention and to better distinguish the claimed invention from the prior art. Support is found in the original specification. No new matter has been entered.

The rejection of claims 1, 2, 4, 5, and 7-10 as obvious from Callis is rendered moot by the cancellation of all of said claims. Moreover, it is submitted the new claims are patentably distinguished over Callis and any of the other art of record.

In the prior art, it is well known that ethanol-blended gasoline has to be substantially free of water, i.e., the water content ratio therein has to remain less than 0.1 vol%. This fact is supported the following document:

Article "Technical Issues in Production and Delivery of Ethanol-Blended Gasoline" (Appendix A) http://www.env.go.jp/earth/ondanka/renewable/02/

(The 2nd Meeting of the Conference for Promoting the Utilization of Renewable Fuels, Ministry of the Environment, Government of Japan)

In paragraph 3 of the above article (Appendix A), it is reported:

"…when this phenomenon which is called phase separation occurs, ethanol partly gets out of gasoline, hence the predetermined quality of gasoline can no longer be maintained. For example, the octane value becomes lower or the distillation characteristics change, leading to failure to maintain the predetermined quality of gasoline in extreme cases. Therefore, the phenomenon of phase separation is never allowed in ethanol-blended gasoline."

In paragraph 4 of the above article (Appendix A), it is reported:

"…In the case where ethanol-blended gasoline contains ethanol at a dose of 3 vol%, it is estimated that the solubility of water is about 0.1 vol% (1,000 vol ppm) at nearly ambient

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temperature, and it is conceivable that phase separation will occur when water is aduterated at levels exceeding that level."

In order to avoid any possible overlap, the claims have been amended to delete any reference to methanol. The aluminum corrosion inhibitors (additives) used in the present invention are completely distinct from those disclosed in the prior art.

The instant aluminum corrosion inhibitors used in the present invention are <u>completely different</u> in not only their actions and advantageous effects but also their ingredients from the prior art corrosion inhibitors which have been added to the prior art <u>gasoline</u> fuels.

The corrosive reaction of aluminum by <u>dry</u> corrosion is chemically different from the phenomena observed in connection with Fe metal corrosion including the formation of red rust, which is a kind of wet corrosion.

As pointed out in our earlier Amendments, incorporated herein by reference, the corrosion of aluminum, which is a problem to be solved in the present invention, is a dissolution phenomenon of aluminum by production of aluminum alkoxides as a result of reaction of an aluminum metal with an alcohol. Since this alkoxide reaction is a chemical reaction, the aluminum will corrode and disappear in as little as one day under certain conditions once the reaction has been initiated, as demonstrated in Working Examples of the Specification.

In contrast, the target metal of the prior art "corrosion inhibitors" which are added to gasoline is <u>iron</u>, an embodiment of which is a "steel plate" or "steel sheet or strip" product (such as steel plate, lead-tin coated (galvanized); steel plate, zinc coated (galvanized); and steel plate, tin-zinc coated (galvanized)), used in fuel tank applications.

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The corrosion that occurs in the case of prior art iron based fuel tanks is based on the following phenomenon:

> while the fuel is exposed to air in the fuel tank, the moisture in the air is incorporated into the fuel, thereby resulting in separation of water drops from gasoline, followed by accumulation of water on the bottom of the fuel, whereby water is brought into contact with the steel plate so that it will take several years to induce this corrosion (the formation of red rust).

The corrosion inhibitors used in the prior art are nitrogen- and/or sulfur-containing polar compounds such as aliphatic amines and sulfonate salts, which are ineffective and inactive in the inhibition of a "aluminum corrosion (alkoxide reaction)" which is the goal of the present claimed invention.

A project sponsored by the Ministry of Economy, Trade and Industry (METI), Japan and the Ministry of Land, Infrastructure, Transport and Tourism (MLIT), Japan, the Japan Automobile Manufacturers Association, Inc. (JMA), Japan, conducted experimental trials for the reaction of aluminum plates after mixing commercially available gasoline with anhydrous alcohol, and reported the same results as in the disclosure on pages 13 to 82 of the English text, and FIGs. 1 to 37.

The fuel additives, as disclosed and claimed in the instant application in the Specification, are quite different from the prior art metal corrosion inhibitors in terms of not only their actions and beneficial effects but also their ingredients.

Moreover, Callis is silent about the prevention of "aluminum corrosion issues", caused by the alkoxide reaction (at an elevated temperature of from 80°C to 120°C) of an aluminum or

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aluminum alloy fuel delivery pipes and other aluminum or aluminum alloy parts with the alcohol contained in the fuel composition.

See also the Inventor's article, Corrosion Engineering 53, pp.71-80 (2004) (Appendix B), which supports the unique features of the present invention.

Considering specifically the Callis patent, Callis et al. lists four components for his liquid motor fuel:

(1) hydrocarbons (HC),

(2) low molecular weight alcohols,

(3) C5 or higher saturated aliphatic ethers, and

(4) higher molecular weight alcohols,

wherein water may or may not be contained.

The instant claimed fuel compositions are novel and non-obvious over Callis because the inventive fuel compositions as set forth in the new claims lack ether while containing other additives not taught by Callis.

For ethanol-blended gasoline, it is well known that phase separation is a major problem and it is absolutely necessary to avoid the occurrence of fuel phase separation (Appendix A). Phase separation could cause most of the ethanol and water to separate from the bulk fuel and drop to the bottom of the tank, leaving gasoline with a significantly reduced level of ethanol in the upper phase. If the lower phase of water and ethanol is large enough to reach the fuel inlet, it could be pumped directly to the engine and cause significant problems. Even if the ethanol water phase at the bottom of the tank is not drawn into the fuel inlet, the reduced ethanol level of the fuel reduces the octane rating, which could result in serious and even catastrophic engine problems without warning.

Therefore, it is well known that the phase separation will occur when water is blended at a dose exceeding 0.1 vol% in the ethanol-blended gasoline. In other words, it is believed that gasoline containing ethanol is essentially free of water (or holds at most 0.1 vol% water) in the prior art.

In the Office Action, the Examiner states that "It is obvious to one having ordinary skill in the art at the time the invention was made that the fuel composition of CALLIS has water being added to the composition since it is known in the art that hydrocarbon components and alcohols usually contain slight amounts of water (Page 3, Line 2 from the bottom to Page 4, Line 3 of the Office Action).

Applicant respectfully submits that Callis is completely silent regarding aluminum dry corrosion inhibition by water. It is also believed to be incorrect that hydrocarbon components and alcohols usually contain slight amounts of water (i.e., it is not inferable that a liquid hydrocarbon component-alcohol fuel composition contains water at an amount equal to either (1) $0.002 \times N$ wt.% or more or (2) 0.1 wt.% or more of the resulting liquid fuel composition, provided that the larger amount of admixed water is selected between said (1) $0.002 \times N$ wt.% or more and said (2) 0.1 wt.% or more of the resulting liquid fuel composition), or required by Applicant's claims.

Accordingly, it is submitted that the claims cannot be said to be obvious from Callis.

Having dealt with all the objections raised by the Examiner, the Application is believed to be in order for allowance. The Examiner is respectfully requested to telephone the undersigned attorney to discuss any issues remaining after entry of the foregoing Amendment.
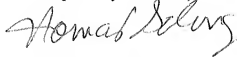
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Extension fee and additional independent claim fee are being paid via EFS WEB in the amount of $175.00.

In the event there are any fee deficiencies or additional fees are payable, please charge them (or credit any overpayment) to our Deposit Account Number 08-1391.
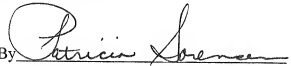
Respectfully submitted,

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CERTIFICATE OF ELECTRONIC FILING

I hereby certify that this paper is being deposited with the United States Patent Office via the electronic filing procedure on _December 7, 2009_ at Tucson, Arizona.

By _Patricia Sorensen_

NPS:sb:ps

U.S. PATENT APPLICATION SERIAL NO. 10/539,080

FILED: JUNE 15, 2005

APPENDIX A

<u>Filed with Amendment C</u>

PARTIAL TRANSLATION OF ARTICLE

"Technical Issues in Production and Delivery of

Ethanol-Blended Gasoline"

DOCKET: SHIG CP22JU03SG

SERIAL NO. 10/539,080

APPENDIX A

Technical Problems in Production of Ethanol-Added or Ethanol-Blended Gasoline and Its Distribution Process

1.   In the case where we imagine to produce ethanol-added or ethanol-blended gasoline in a refinery blender plant, similarly to the one in an existing gasoline production plant, the product gasoline may be qualitatively deteriorated due to absorption of moisture (adulteration with water) or contamination in the subsequent distribution process (transportation, storage) and, in extreme cases, the gasoline may possibly become a substandard one or have a risk of exerting an adverse influence on the automotive engine, so that the existing production and distribution methods cannot be applied as far as ethanol-blended gasoline is concerned.

2.   Currently, it is difficult to completely prevent adulteration with water (absorption of moisture) in the equipment (transportation and storage means) currently in use in gasoline distribution and, in the existing circumstances, the gasoline is always in contact with moisture (water) in the process of distribution, though at low levels.   In the case of petroleum-derived gasoline, however, the content of dissolved water is about 100 to 200 ppm by weight (wtppm), and its contacting with water generally produces no problem since the quality of gasoline is not affected even upon separation of water.

3.   On the other hand, when ethanol-blended gasoline gets adulterated with water, in particular at levels exceeding the limit of solubility, free water can exist and, on that occasion, the phenomenon of a considerable proportion of the ethanol mixed   with gasoline being transferred to the aqueous phase occurs because of higher affinity of ethanol, which is a polar compound, for water than for gasoline.   When this phenomenon which is called phase separation occurs, ethanol partly gets out of the gasoline, hence the predetermined quality of gasoline can no longer be maintained.   For example, the octane value becomes lower or the distillation characteristics change, leading to failure to maintain the predetermined quality of gasoline in extreme cases.   Therefore,

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the phenomenon of phase separation is never allowable in ethanol-blended gasoline.

①Gasoline + 1% water ②Gasoline + 10% water ③E10 + 1% water ④E10 + 10% water

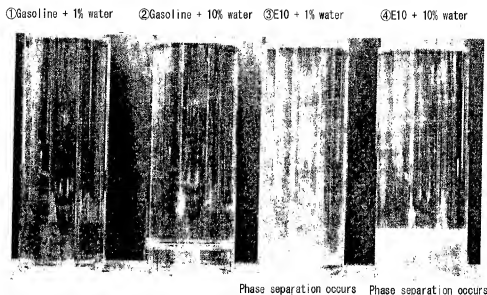Phase separation occurs   Phase separation occurs

Fig. 1:   Phase separation in ethanol-blended gasoline

(While admixing of water with gasoline results only in liberation of water, admixing of water with ethanol-blended gasoline results not only in transfer of water but also in transfer of ethanol contained in gasoline into the water phase, causing phase separation.)

4.   According to the technological data provided by ADM, USA, the solubility of water in ethanol-blended gasoline is as shown below in Fig. 2, though it varies depending on the level of blending of ethanol and on the temperature.
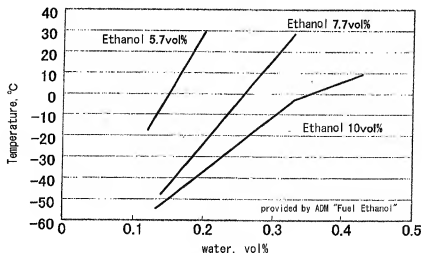
Fig. 2:   Solubility of water in ethanol-blended gasoline

Fig. 2 shows the data for the cases of ethanol contents of 5.7 to 10vol%.   In
the case where ethanol-blended gasoline contains ethanol at a dose of 3vol%, it is esti-
mated that the solubility of water is about 0.1vol% (1,000 volppm) at nearly ambient
temperature and it is conceivable that phase separation will occur when water is adulte-
rated at levels exceeding that level.

環境省再生可能燃料利用推進会議資料

エタノール混合ガソリンの製造、及び流通における技術課題

1. エタノール混合ガソリンを、現在のガソリン製造方法と同様に製油所のブレンダー設備において製造することを想定した場合、その後の製品ガソリンの流通過程（輸送、貯蔵）における水分混入、汚れ混入によってガソリン品質が悪化し、著しい場合にはガソリン品質が規格外れとなる、あるいは自動車エンジンに悪影響を及ぼす危険性があるため、エタノール混合ガソリンにおいては現状のガソリンの製造、流通方法をそのまま適用することは出来ない。

2. 現在、ガソリンの流通過程において使用されている設備（輸送手段、貯蔵設備）においては、完全に水分混入を防止することは困難であり、現状では、ガソリンは流通過程においてわずかではあるが水分と接触している状況にある。しかし、石油系由来のガソリンにおいては、水分溶解量は約100～200wtppm であり、また、水分が析出した場合でも特にガソリン品質に影響することはないため、水分との接触は一般的には問題とならない。

3. 一方、エタノール混合ガソリンに水分が混入、特に溶解可能限界を超えて混入する場合には遊離水分が存在する事になるが、この時、エタノールは極性化合物でありガソリンよりも水に対する親和性が高いことにより、ガソリンに混合されたエタノールのかなりの割合が水相へ移行するという現象が起きる。この現象は相分離と呼ばれているが、相分離が発生するとガソリンからエタノールが抜け出すため、設定した品質が保てなくなる。例えば、オクタン価の低下、蒸留性状の変化などが起こり、著しい場合にはガソリン規格を外れることになる。そのため、エタノール混合ガソリンにおいて相分離は絶対に起こしてはならない現象である。 A

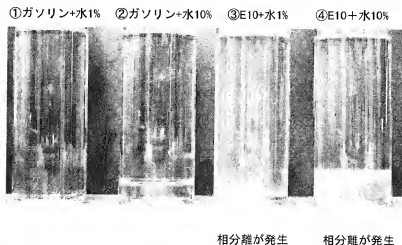①ガソリン+水1%　②ガソリン+水10%　③E10+水1%　④E10+水10%

相分離が発生　　相分離が発生

図1　エタノール混合ガソリンの相分離
（ガソリンに水を混合した場合には水が遊離するだけであるが、エタノール混合ガソリンに水が混合した場合には、水だけではなくガソリン中のエタノールまで水に移行して相分離が起きる）

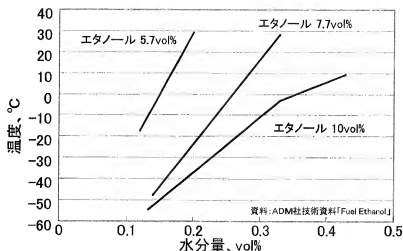4. エタノール混合ガソリンの水分溶解量は、混合するエタノール量、および温度によって異なるが、米国 ADM 社の技術資料によれば図2に示すとおりである。

図2　エタノール混合ガソリンの水分溶解量

　図2にはエタノール混合割合が 5.7 〜10vol%の場合が記載されているが、エタノール3vol%混合ガソリンの場合においては、水分溶解量は常温付近で 0.1vol%（1,000volppm）程度であると推定され、これを超える水分が混入した場合には相分離を起こすと考えられる。

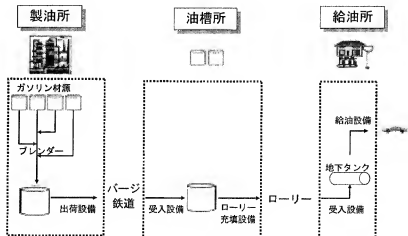5. 日本における現状の最も一般的なガソリン流通経路は図3に示すとおりである。なお、一部は油槽所を経由せずに製油所から直接ローリー出荷されるものもある。

図3　日本における現状の一般的なガソリン流通経路

製油所のガソリン混合時から給油所での販売までに、いくつかの輸送手段、貯蔵設備を経由しているため、給油所での販売に至るまでに水分の混入を防止してエタノール混合ガソリンの相分離を起こさずに流通させることはきわめて困難と推定される。

6. エタノール混合ガソリンは石油系ガソリンと溶解性が異なり、極性物質を溶解、分散させ易い性状を有しており、配管、貯蔵タンクから汚れを溶解、分散させる可能性がある。

7. 米国等においては、これらの水分混入、汚れ混入を防止するため、エタノール混合ガソリンの製造を製油所ブレンダーではなく、主に油槽所におけるローリー出荷ポイントで行っている。すなわち、製油所においてはエタノールを除くガソリン基材を混合してサブオクタンガソリンを製造してこれを油槽所へ輸送する。一方、燃料エタノールはエタノール製造工場より油槽所へ輸送する。油槽所においては、サブオクタンガソリンと燃料エタノールをラインブレンド装置により混合し、直ちにローリーへ充填して出荷している。これらの状況を図4、図5に示す。

　ラインブレンド装置にはいくつかのタイプがあるが、米国カリフォルニア州の油槽所においては、コンピューター制御により混合中に混合比率を常に一定とするレシオコントロール法を使用して、混合割合の信頼性を保っている。
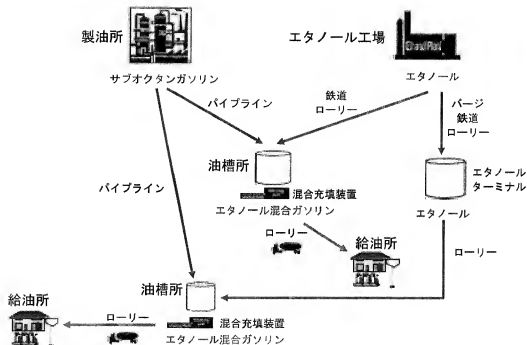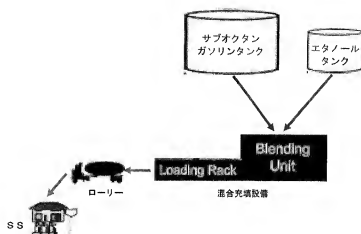

図4　米国におけるエタノール混合ガソリンの供給方法

図5 米国油槽所におけるエタノール混合ガソリンの製造方法

8. 米国においては、1980年代より主として中西部においてエタノール10vol%混合ガソリン（E10ガソリン）が使用されていたが、最近ではリフォーミュレイテッドガソリン（RFG）の含酸素化合物をMTBEからエタノールへ変更する州が増大していることにより、エタノール混合ガソリンの使用が増大している。

特に、カリフォルニア州においては、これまではほとんどエタノール混合ガソリンが使用されていなかったが、2003年末にMTBEの使用が禁止されることになったために、昨年から今年にかけて、MTBE混合ガソリンからエタノール混合ガソリンへの変更への対応が行われている。

9. カリフォルニア州の石油会社がエタノール混合ガソリン導入において行った対応は以下のとおりである。

　①エタノール配送ルートの新設
　　・主として中西部のエタノール工場から鉄道、船で燃料エタノールを輸送するための燃料エタノール受け入れ設備、及び油槽所への配送ルートの新設

　②すべての油槽所に次の設備を設置
　　・エタノール受け入れ設備の新設（鉄道、ローリー）
　　・エタノール貯蔵タンクの新設、改造
　　・混合充填設備の新設
　　・エタノール対応消火設備の新設

③給油所における水分管理の徹底
  ・エタノール混合ガソリン導入時には給油所地下タンクの完全清掃
  ・導入後は日常的な水分管理の実行

10. 油槽所出荷ポイントにおけるエタノール混合ガソリンの製造を行った場合、製造したエタノール混合ガソリン(最終製品)をサンプリングして品質確認を行うことが困難であるという問題がある。

現在の品質確保法では、給油所においてユーザーに渡る時の品質を保証しているものであるが、出荷ポイントでの混合でエタノール混合ガソリンを製造し、そのままローリーで出荷される場合に、製品の品質をどのように保証するかが課題となる。

カリフォルニア州においては、製品品質の確認をエタノール混合ガソリン(最終製品)によるのではなく、混合材源であるサブオクタンガソリンと燃料エタノールの性状、および混合割合から算出する方法を採用している。

11. 日本においてエタノール混合ガソリンを導入する場合には、以下の設備対応が必要である。

①製油所ブレンダーにおける製造は水分混入、及び汚れ混入の恐れがあるため不可能であると考えられる。このため、米国などと同様に製油所、油槽所の出荷ポイントにおけるラインブレンド方式への変更を行う必要があり、これに必要な対応設備を設置する必要がある。

②給油所地下タンク、給油機についてエタノール混合ガソリンへの設備対応を行う必要がある。

③輸送手段(船、タンク車、ローリー)についてエタノール混合ガソリンへの設備対応を行う必要がある

また、その他の課題として、以下の対策が必要である。

①エタノール混合ガソリン(最終製品)ではなく、材源性状(サブオクタンガソリン、燃料エタノール)と混合比率からの計算値による品質管理体制への変更(品質確保法関連)

②油槽所においてガソリン混合を行うことに伴う揮発油税課税システムの見直し(揮発油税法関連)

③輸送手段(船、貨車、ローリー)、給油所(地下タンク)における日常的な水分管理の実施

④アルコール類に係る消防法上の基準・消火設備対応(消防法関連)

12. 日本においては、製油所と油槽所の両方から製品ガソリンの出荷をおこなっているため、製油所と油槽所の出荷ポイントにおいて混合出荷設備の設置が必要である。また燃料エタノールは海外からの輸入となるために製油所に輸入エタノール受入れ設備（エタノール輸入基地）の設置が必要である。
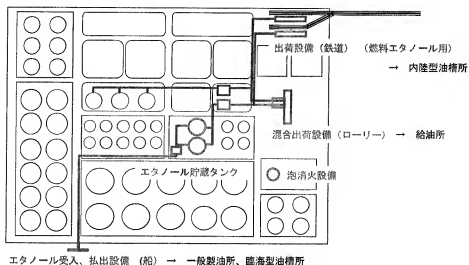
製油所においては以下の設備対応が必要である。

図6　製油所における必要設備

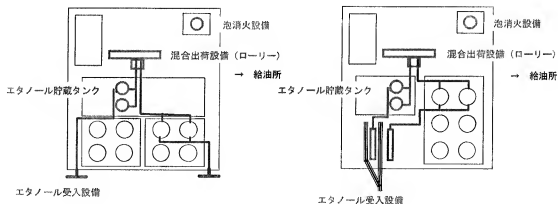13. また、油槽所においては以下の設備対応が必要である。

図7　油槽所における必要設備
（左：臨海型油槽所、右：内陸型油槽所）

14. 日本には、製油所は約30ヶ所、油槽所は約230ヶ所、給油所は約50,000ヶ所あり、各設備においてエタノール混合ガソリン導入に必要な対応設備仕様を検討した上で設置、改造を行う必要がある。また、これらの対応設備の設置により、問題のない品質のエタノール混合ガソリンがユーザーまで供給できるかについて実証試験を行って確認しておく必要がある。

15. 以上述べたように、エタノール混合ガソリンの導入は大幅なガソリン製造、流通設備の変更を必要とするものであり、また、製品品質保証体系の変更、揮発油税課税システムの見直しなどの検討を必要とするなど多くの課題を有している。
　地球温暖化対策の手段としてエタノール混合ガソリンを評価する場合には、これらに加えて、燃料エタノールの供給安定性、CO_2 削減方法としての費用対効果などを検討してエタノール混合ガソリン導入のメリット、デメリットを十分明確にした上で実施を検討すべきであると考えられる。

エタノール混合ガソリンの製造、及び流通に伴う課題（まとめ）

1. 品質上の課題
    ◎水分混入による品質悪化（相分離）
    ◎汚れ混入による品質悪化

2. 設備上の課題
    ◎燃料エタノール配送網の設置
    ◎製油所、油槽所の出荷ポイントでのエタノール混合設備の設置
    ◎輸送手段（船、貨車、ローリー）のエタノール対応
    ◎給油所設備（地下タンク、給油機）のエタノール対応

3. システム上の課題
    ◎製品品質保証システムの変更
    ◎揮発油税課税システムの変更

　バイオ燃料の自動車燃料への導入は、費用対効果において地球温暖化対策の選択肢として疑問があるが、仮にバイオ燃料の自動車用燃料への導入が余儀なくされた場合には、ガソリンに性状が似通っており技術的により問題点の少ないETBE利用についても有力な代替案として比較検討すべきである。

　すなわち、エタノール混合ガソリンが製油所、油槽所、給油所、及び輸送手段において大幅な設備変更、改造を必要とするのに対して、ETBEを利用する場合にはこれらの設備変更を必要としない。石油会社はMTBEをガソリン材源として使用した実績があり、ETBE混合ガソリンの利用は容易である。また、ETBE混合ガソリンはエタノール混合ガソリンよりもガソリン品質として優れており、自動車エンジンに与える悪影響はほとんどない。

　ETBEはエタノールとイソブチレンを原料として製油所で製造することができ、エタノール相当分は再生可能燃料と見なすことが出来る。ETBEの製造可能量はイソブチレン生産量により制約を受けるが、現状の石油精製設備からはETBE混合量として約4vol%（エタノール換算約2vol%）が生産可能である。今後、n－ブタンからイソブチレン製造するプロセスが経済的に導入できるようになれば、さらに増産できる可能性もある。

　したがって、ETBEは量的な制約はあるものの、ETBE導入ケースについても詳細な検討が必要であると考えられる。

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APPENDIX B

Filed with Amendment C

Corrosion Behavior of Aluminum in Mixed Alcohol Solutions

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Anhydrous alcohol reacts with aluminum at high temperatures to form aluminum alkoxide. There are no reports on the reaction when a mixture of two or more alcohols is used, but it is known that the addition of minute quantities of water will prevent the alkoxide reaction. This paper describes (1) the reaction of aluminum with a number of mixed alcohol solutions near the azeotropy point, and (2) the minimum water concentration in a mixed alcohol solution that will prevent the alkoxide reaction.

Pieces of pure aluminum (JIS-A1085) were reacted in a vessel made from SUS304 with 50 m*l* of each a range of mixed alcohol solutions. The solutions were prepared from different combinations of five kinds of 2-4 carbon alcohols: ethanol, *n*-propanol, isopropanol, *n*-butanol, and isobutanol. The reactions were carried out for 72 hours each at 353K, 373K and 393K respectively. The results showed that the reactions with mixed alcohol solutions took place at lower temperatures than those with single-alcohol solutions. The minimum water concentration that prevented the alkoxide reaction was higher for mixed alcohol solutions than for single-alcohol solutions. Considering these results from the standpoint of the dissolution phenomenon of alcohol, I postulated that the size, structure, and stability of the alcoholic clusters in mixed alcohol solutions are important factors contributing to the reaction.

1. INTRODUCTION

Industrial usage of alcohol is expected to increase substantially as new automobile fuels, solvents, and raw materials are developed, and the share of Al is also rising because of the need to reduce the weight of vehicle bodies. It seems quite probable, therefore, that alcohol and Al will be in contact in severe service conditions. At ambient temperature, alcohol is inert to Al, but at elevated temperatures anhydrous alcohol reacts with Al to produce aluminum alkoxide. Little is known, however, about the corrosion process of Al (i.e., the formation of aluminum alkoxide) in reaction with mixed alcohol. The study discussed in this paper investigated the reaction of Al with mixed alcohol in order to elucidate the mechanism of alkoxide formation.
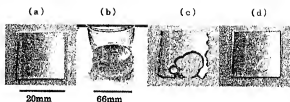
Fig. 1
Samples of an aluminum test piece (a), the solution after test (b),
the corroded piece (c) and the piece which did not react. (d).

The article that follows briefly reviews the process whereby aluminum alkoxide is synthesized and outlines its characteristic features. Aluminum alkoxide (alcolate) is classified as an ester aluminate. It is synthesized through the following reactions [1]:

(1) reaction of Al and alcohol in presence of HgCl
(2) adding excess alcohol to organic solution of aluminum chloride
(3) reaction of Al powder with alcohol at elevated temperature

Aluminum alkoxide is expressed as $Al(OR)_3$ where R may be alkyl or aryl (usually alkyl). Aluminum ethylate in excess ethanol solution yields acid by forming complex ion through the reaction [2]

$$Al(OC_2H_5)_3 + C_2H_5OH \rightarrow [Al(OC_2H_5)_4]^- H^+ \qquad (1)$$
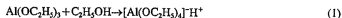
Depending on the type of alkyl, $Al(OR)_3$ may exist either in liquid, solid, or wax form at ambient temperature. When left in an atmospheric environment at ambient temperature, aluminum alkoxide is disintegrated by hydrolysis to yield alumina and alcohol.

Trace water impurity in ethanol is said to retard the alkoxide reaction of Al [3,4]. There is no report on the quantitative relation of the three factors in the alkoxide reaction of Al: mixed alcohol, water impurity level, and temperature.

To fill this information gap, we reacted Al and alcohol for 72 h using alcohols with carbon numbers 2-4 either in a pure state or in one of five alcohol mixtures at varying levels of water impurity and at three temperatures: 353 K, 373 K, and 393 K.

2. EXPERIMENT

2.1 Al specimen and alcohols

A $20 \times 20 \times 1$ mm Al test piece (Fig. 1 (a)) was cut out of as-received sheet of industrially pure Al (A1085 defined in JIS with purity > 99.85%).

The following five types of alcohol with carbon numbers 2-4 were used for the test: EtOH (ethanol) for alcohol with carbon number 2 (Nihon Alcohol Sales Corp.; EtOH > 99°), NPA (normal propanol; GODO Solvent Corp.; industrial grade) and IPA (isopropanol; GODO Solvent Corp.; industrial pure grade) for alcohols with carbon number 3, NBA (normal butanol; GODO Solvent Corp.; industrial 99% grade), and IBA (isobutanol; GODO Solvent Corp.; industrial pure grade).

Table 1
Single alcohol solutions boiling point and volume ratio.

Alcohol	b.p.(K)	Volume ratio (%)				
		1-1	1-2	1-3	1-4	1-5
EtOH	351.5	100				
NPA	370.4		100			
IPA	355.6			100		
NBA	390.7				100	
IBA	381.1					100

Table 2
Two-alcohol solutions volume ratio.

Alcohol	Volume ratio (%)									
	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8	2-9	2-10
EtOH	50	50	50	50						
NPA	50				50	50	50			
IPA		50			50			50	50	
NBA			50			50		50		50
IBA				50			50		50	50

Table 3
Three-alcohol solutions volume ratio.

Alcohol	Volume ratio (%)									
	3-1	3-2	3-3	3-4	3-5	3-6	3-7	3-8	3-9	3-10
EtOH	33	33	33	33	33	33				
NPA	33	33	33				33	33	33	
IPA	33			33	33		33	33		33
NBA		33		33		33	33		33	33
IBA			33		33	33		33	33	33

Table 4
Four-alcohol solutions volume ratio.

Alcohol	Volume ratio (%)				
	4-1	4-2	4-3	4-4	4-5
EtOH	25	25	25	25	
NPA	25	25	25		25
IPA	25	25		25	25
NBA	25		25	25	25
IBA		25	25	25	25

Table 5
Five-alcohol solutions volume ratio.

| Alcohol	Volume ratio (%)
	5-1
EtOH	20
NPA	20
IPA	20
NBA	20
IBA	20

The purity of these pure alcohol samples was measured by gas chromatography (GC-FID) and gas chromatograph mass spectroscopy (GC-MS) using an instrument manufactured by SHIMADZU; these checks confirmed that the purity was at least 99.9 vol%. The water impurity levels in these pure alcohol samples, ascertained using GC-MS with reference to the calibration line, were no more than 0.1 vol%. A controlled amount of ion-exchanged water with electric conductivity of 0.1 μS/m was used to control the water impurity levels of these pure alcohol samples,.

Table 1 shows the boiling point of five pure alcohol samples. Tables 2-5 show the volumetric ratios of the alcohol mixtures used for the test.

2.2 Reaction apparatus and experimental procedure

The reactor was an SUS304 container with a capacity of about 400 m*l* (external diameter 90 mm, depth 90 mm, wall thickness 5 mm; Fig. 2). The experimental procedure was as follows:

(1) The reactor chamber was thoroughly dried in a thermostatted chamber kept at 373 K, covered with a lid to prevent adsorption of water from the atmosphere. The test container was cooled down to ambient temperature. and 50 m*l* of mixed alcohol solution containing from 0 to a few% water impurity was poured into it. The volume of alcohol was measured with a pipette, and
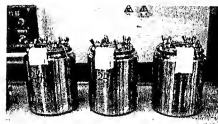
90mm

Fig. 2
Appearance of the SUS304 ball mill.

the amount of ion exchange water added to the alcohol was measured with a gas-tight syringe (maximum capacity 1 m*l*) to ensure a water impurity precision level of 0.1 vol%.

(2) An Al test piece washed with ethanol and dried was placed in the reaction chamber containing 50 m*l* alcohol after its dry weight was measured.

(3) The influence of oxide film formed on the Al test piece was eliminated by introducing 3-4 lines of scratches with a metal rasp. This operation was done for the Al test piece immersed in the alcohol test solution to prevent oxidation of the scratched surfaces.

(4) Oxidation of alcohol during the test period was minimized by purging the air in the test chamber over the alcohol solution with N$_2$ gas before placing the lid on the chamber and fastening to the chamber body with screws.

(5) As many as five test containers were placed on the upper stage of the thermostatted chamber set at either 353 K, 373 K, or 393 K. The temperature in the chamber was measured using a thermocouple.

(6) The test containers were removed from the thermostatted chamber after a specified period (72).

(7) The test chamber lid was opened for a visual inspection of the state of the Al test piece and the alcohol test solution.

(8) If the visual inspection found that the Al test piece had not degraded, it was removed from the alcohol solution, dried and weighed. If, on the other hand, the Al test piece had disintegrated because of corrosion, the test solution conditions (color, viscosity and presence or not of sediment) were registered. If a residue of the corroded Al test piece was present, the corrosion product layer was removed from it, washed in water, dried, and weighed to register the weight loss during the immersion.

Following our firm's criterion, the Al test piece was classified as subjected to corrosion when the weight loss exceeded 0.3 mass% or when pitting or discoloring was detected by visual inspection.

3. RESULTS

In the experiments at 393 K, all the test pieces disappeared after the 72 h immersion due to completion of the alkoxide reaction. The alcohol solution showed such modifications as white turbidity, floating particles, solid deposit, and a rise in viscosity (Fig. 1 (b) shows alcohol solution with white turbidity). In the case where the Al test piece corroded, the number of floating solid
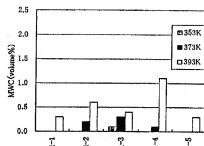
Fig. 3
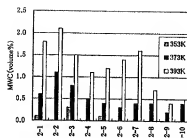The MWCs for single alcohol solutions at different temperatures.

Fig. 4
The MWCs for two alcohol solutions at different temperatures.

particles in the alcohol solution increased as the level of water impurity in the alcohol test solution rose. These floating particles were suspected of being the hydrolysis product from alcolate synthesized by the alkoxide reaction [2]. At the test temperature of 373 K, one Al test piece remained undissolved, whereas a few remained at 353 K. Figure 1 (c) shows a degraded Al test piece with mass loss of 33%, and Fig. 1 (d) shows an intact Al test piece on which the rasped surface scratches can still be seen. These findings suggested that the rate of alkoxide process was quite fast.

Figure 3 summarizes the results obtained in pure alcohol solutions. The scale of the vertical axis in this plot is MWC (minimum water concentration at which alkoxide reaction was prevented). When the level of added water was greater than MWC, the alkoxide reaction of Al was inhibited in the alcohol solution, but when the water level in the alcohol was lower than MWC, the alkoxide reaction for Al progressed. Figure 4 summarizes the test results for 2-alcohol mixtures, Fig. 5 for 3-alcohol mixtures, Fig. 6 for 4-alcohol mixture, and Fig. 7 5-alcohol mixture. Table 6 reproduces the literature values of the physical properties of aluminum alkoxides with carbon numbers 2-4 [9].
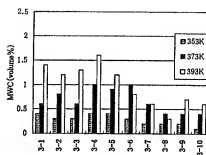

Fig. 5
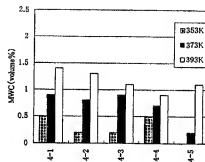The MWCs for three alcohol solutions at different temperatures.

Fig. 6
The MWCs for four alcohol solutions at different temperatures.

Table 6
Physical characteristics of aluminum oxides [9].

Alkoxide	M.W.	state(at R.T.)	m.p.(K)
Al(OC$_2$H$_5$)$_3$	162.3	solid	412
Al(O-n-C$_3$H$_7$)$_3$	204.2	solid	380
Al(O-i-C$_3$H$_7$)$_3$	204.2	solid	461
Al(O-n-C$_4$H$_9$)$_3$	246.3	solid	377
Al(O-i-C$_4$H$_9$)$_3$	246.3	solid	482

With reference to Fig. 3 and Table 6, it seems allowable to say that MWC at 393 K rises with the decreasing melting point of alcohol.

On the other hand, Figs. 4-7 indicate that MWC rises with the rising temperature, excluding cases (3-6) and (3-8), for the 3-alcohol mixtures. Note too that mixing of alcohols tended to make MWC rise and the alkoxide reaction initiation temperature drop.

Ethanol is a promising mixing constituent for automobile fuel (gasoline). Pure anhydrous ethanol did not yield an alkoxide reaction up to 373 K. When mixed with other alcohols, however, anhydrous ethanol yielded alkoxide reactions at 353 K and pushed MWC to higher levels than were reached by the other combinations of alcohols.

4. DISCUSSION

As is generally acknowledged, the mutual solubility behavior of non-electrolytes depends largely on molecular geometry and interatomic interaction. Polar molecules like alcohol, water, and acetic acid are subject to auto-association that yields 3D (three-dimensional) structures (clusters) [1,5]. Some alcolates formed from certain types of alcohol are known to be insoluble. We analyzed the experimental evidence in respect to the physical and chemical properties and thermodynamic stability of alcolate (macroscopic viewpoint) and also in respect to the stability of mixed alcohol clusters, which are completely miscible with no phase separation (microscopic viewpoint).

4.1 Properties of alcolate and alkoxide reaction

The actual state of existence of aluminum alcolate in alcohol solution is expressed by [Al(OR)$_3$]$_n$ (R: alkyl, n: 3-5), showing a trend of rising n with the decreasing R. For example, for R = C$_2$H$_5$, Al is associated in tetrahedral form. Bear in mind that alcolate formed from alcohol of greater molecular weight does not necessarily form larger clusters. This can be readily understood from Table 6, which shows that the boiling point of alcolate does not rise with increasing molecular weight. One must also note that aluminum ethylate is insoluble to ethanol, but aluminum isopropylate is soluble in IPA [9]. The results summarized in Fig. 3 can be explained reasonably with reference to the evidence just outlined. When the alcolate formed through the alkoxide reaction was soluble in the alcohol solution (case 1-3 in Fig. 3), the alkoxide reaction would proceed readily, whereas when the formed alcolate existed in solid form (or as precipitate on the Al test piece), the alkoxide reaction would be retarded due to reduced coverage of the Al surface with the alcohol solution by the formed alcolate solid. The latter situation is represented by case 1-1 in Fig. 3, in which the formed alcolate was solid at temperatures lower than 393 K and insoluble to ethanol.

The preceding consideration is based on macroscopic properties. Microscopic factors will be considered next: the effect of mixing with anhydrous alcohol on corrosion reaction temperature in
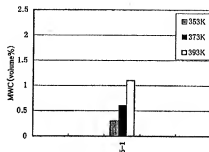
Fig. 7
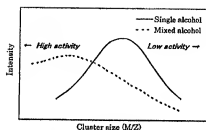The MWCs for five alcohol solutions at different temperatures.

Fig. 8.
Image illustrating the difference in cluster size distribution between a single alcohol solution and a mixed alcohol solution.

sec. 4.2, and the mechanism by which alcohol with water impurity retards the alkoxide reaction in sec. 4.3.

4.2 Reducing corrosion reaction temperature by adding anhydrous alcohol

Whether new cluster will form on the addition of unlike alcohol in alcohol solution depends on the mutual miscibility of the unlike alcohol molecules. From the thermodynamic perspective, if the mixing of unlike alcohols yields no heat (i.e., is athermal), the solution is considered to result from the entropy effect [5]. For the spontaneous solution to take place under constant temperature and pressure, the Gibbs free energy change ΔG must be negative

$$\Delta G = \Delta H - T\Delta S < 0 \qquad (2)$$

where ΔH is the enthalpy change, ΔS is the entropy change, and T is the absolute temperature. In the case of athermal dissolution, $\Delta H = 0$; therefore

$$\Delta G = -T\Delta S < 0 \qquad (3)$$

Accordingly, ΔS must be positive. This means that if mixing two or more unlike alcohols in a solution yields no heat and no phase separation, the solution's degree of disorder must increase. In other words, the clusters of the mixed alcohols must be smaller than those in pure alcohol solution.

The conclusion derived by a thermodynamic consideration of the alcohol mixture can also be explained in terms of the stability of the clusters (3D structure) depending on the size of the alcohol molecules and the polarity. In pure alcohol solution, molecular size and polarity are both homogeneous, so a stable 3D structure will grow, yielding relatively large clusters [2]. On the other hand, in a mixture of unlike alcohols, differences between alcohol molecular species in respect to 3D structure, polarity, and kinetic energy may prevent stable cluster growth. Correspondingly, the microstructure of an alcohol mixture might be represented by clusters of diminished size or even a single molecular state (see Fig. 8). This would explain why the alkoxide reaction temperature is lower for the mixed alcohols (smaller clusters) than for the pure alcohol (larger clusters).
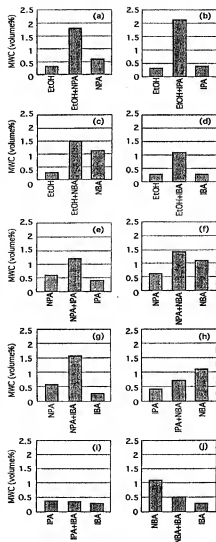
Fig. 9

Comparison showing the MWC for individual alcohols in single solution and their combination in a two-alcohol solution. In cases (a) to (g), the MWCs for the mixture were higher than for each alcohol in single solution. In cases (h) to (j), the MWCs for the mixture were equal to the mean MWC for the individual alcohols in single solution.
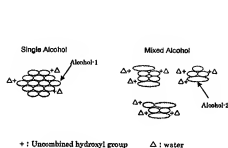
+ : Uncombined hydroxyl group   △ : water

Fig. 10
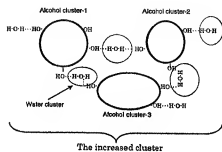Image illustrating a proposed mechanism
of activity loss.

Fig. 11
Image illustrating the size increase in
clusters in a mixed alcohol solution due to
water (molecular or cluster) attachment.

4.3 Rise in MWC from mixing of unlike alcohols

Figure 9 summarizes the observed MWC values for the 2-alcohol mixtures at 393 K for 72 h. As reviewed in section 3, the MWC value of the mixed alcohols was generally higher than that of the respective component except for cases (h), (i), and (j). This apparently irregular result was interpreted in terms of clusters.

We reasoned that the loss of activity of alcohol toward the alkoxide reaction due to the addition resulted from the formation of a hydrogen bond by H_2O to $OH-$ in alcohol (the active point for the alkoxide reaction). Assuming this, we first considered the mechanism of the rise in MWC caused by mixing unlike alcohols. As reviewed in sec. 4.2, the clusters in a mixture of alcohols are smaller than those in pure alcohol, and in consequence the population of free $OH-$ would be higher in the alcohol mixtures than in the pure alcohol. To cancel the reactivity of $OH-$ by water impurity, more water would be needed for an alcohol mixture than for pure alcohol. For example, if each cluster possessed three non-bonded $OH-$ groups for hydrogen bond formation with H_2O, it would take three H_2O molecules for the alkoxide reaction to lose activity for this cluster in pure alcohol, but nine H_2O molecules would be necessary for an activity loss in the alcohol mixture with clusters of refined size (Fig. 10). In this condition, H_2O acts as a glue to combine refined alcohol clusters. Thus, a water impurity would enlarge the clusters in an alcohol mixture, resulting in activity loss (see Fig. 8), and adding unlike alcohol and water to an alcohol solution would synergetically retard the alkoxide reaction (see Fig. 11). The dependence of MWC realized by different combinations of unlike alcohol species may be a factor of the size of the formed cluster on mixing — that is, the smaller the cluster, the higher the MWC. In terms of thermodynamics, MWC increases if the entropy change ΔS is larger in the positive range under the condition of relatively small ΔH.

As seen in Fig. 9, the MWCs of the alcohol mixtures in cases (h), (i), and (j) fell between those of the respective constituents. This can be explained as follows. The alcohol species in these three cases were IPA, NBA, and IBA. The molecules of these three alcohols are all comparatively large and have relatively similar properties. Mixing these alcohols would not readily lead to reorganized clusters of a more refined size. As a consequence, the MWC of mixtures (h), (i), and (j) fell between the MWCs of the respective constituents.

5. CONCLUSIONS

The alkoxide reactions between Al test pieces and mixtures of alcohols with carbon numbers from 2 to 4 were investigated at three different temperatures, 353 K, 373 K, and 393 K, for 72 h. The following conclusions were drawn.

(1) The alkoxide reaction of Al with mixed alcohols proceeded at a lower temperature than the reaction with anhydrous pure alcohol.

(2) The mixing of alcohols increased the minimum water concentration at which the alkoxide reaction was prevented.

(3) The rising reaction temperature also increased the minimum water concentration.

(4) Consideration of the reaction between Al and mixed alcohols on the basis of alcohol miscibility phenomena indicated that the cluster size, structure, and stability of the mixed alcohols were significant factors controlling the alkoxide reaction.

6. FUTURE PROSPECTS OF APPLICATION OF ALCOHOL MIXTURES

The present study demonstrated that the reaction between Al and alcohol mixtures can be explained in terms of the reaction of Al with clustered alcohol molecules. Wakisaka et al. [6,7] undertook cluster analysis of solutions using a liquid phase cluster mass spectrometer. Dixit et al. [8] characterized the mixing state of water and alcohol using an isotope substitution neutron diffraction technique; they concluded that water and alcohol do not mix on the molecular level. These findings indicate that some macroscopically homogeneous solutions are actually heterogeneous on the molecular scale. These new analytic techniques [6-8] might be of use for characterizing alcohol mixtures. To expand the use of alcohol mixtures in an effective way, mixed alcohols must be subjected to cluster analysis and cluster stability evaluation as well as to thermodynamic evaluations.

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